

Nonequilibrium static diverging length scales on approaching a prototypical model glassy stateAdam B. Hopkins,¹ Frank H. Stillinger,¹ and Salvatore Torquato^{1,2,3,4,5}¹*Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA*²*Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey 08544, USA*³*Department of Physics, Princeton University, Princeton, New Jersey 08544, USA*⁴*Princeton Center for Theoretical Science, Princeton University, Princeton, New Jersey 08544, USA*⁵*Program in Applied and Computational Mathematics, Princeton University, Princeton, New Jersey 08544, USA*

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Maximally random jammed states of hard spheres are prototypical glasses. We study the small wavenumber k behavior of the structure factor $S(k)$ of overcompressed million-sphere packings as a function of density up to the jammed state. We find both a precursor to the glassy jammed state evident long before the jamming density is reached and two associated growing length scales, one extracted from the volume integral of the direct correlation function $c(r)$ and the other from the small- k behavior of the structure factor $S(k)$, that can diverge at the “critical” jammed state. We also define a nonequilibrium index X and use it to demonstrate that the packings studied are intrinsically nonequilibrium in nature well before the critical state is reached. The extension of the results reported in the present work to supercooled atomic-liquid models in which the atoms interact with both repulsive and attractive forces is also discussed.

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I. INTRODUCTION

A sufficiently rapid quench of a liquid from above its freezing temperature into a supercooled regime can avoid crystal nucleation to produce a glass with a relaxation time that is much larger than experimental time scales, resulting in an amorphous state (without long-range order) that is simultaneously rigid [1]. The underlying physics of the glass transition is one of the most fascinating open questions in materials science and condensed-matter physics. Many conundrums remain, including whether the growing relaxation times under supercooling have accompanying growing structural length scales. Essentially, two opposing explanations have emerged to address this question. One asserts that a static structural length scale does not exist and identifies growing dynamical length scales [2–4]. The other contends that there is a static growing length scale of thermodynamic origin [5,6]. In this paper, we present both theoretical and computational results that support an alternative view, namely, the existence of a growing static length scale but one that is intrinsically nonequilibrium in nature.

Our model systems are disordered packings of identical spheres with densities between the freezing transition and the so-called maximally random jammed (MRJ) state [7]. The MRJ state under the strict-jamming constraint is a *prototypical* glass in that it lacks any long-range order but is perfectly rigid (the elastic moduli are indeed unbounded) [8,9]. This endows such packings with special attributes. For example, MRJ packings are hyperuniform [10,11] (i.e., infinite wavelength density fluctuations vanish) with a structure factor $S(k)$ that tends to zero linearly in the wavenumber k , implying quasi-long-ranged negative pair correlations (anticorrelations) decaying as a power law [11]. This large-scale property is markedly different from typical liquids in equilibrium, which tend to exhibit more rapidly decaying pair correlations (including exponential decays).

It has been theoretically shown that hyperuniform point distributions are at an “inverted” critical point; i.e., in contrast to normal fluid critical points, the direct correlation function

$c(r)$, rather than the total correlation function $h(r) \equiv g_2(r) - 1$, with $g_2(r)$ the pair correlation function, becomes long-ranged (decaying more slowly than $1/r^d$, where d is the space dimension and r is the radial distance) [10]. This suggests that the volume integral of $c(r)$ for overcompressed hard-sphere configurations [12] that follow Newtonian dynamics might grow as the MRJ state is approached and ultimately diverge at this *inverted* critical point. In this paper, we show that this not only is the case but that the nonequilibrium signature of quasi-long-range anticorrelations, which we quantify via a *nonequilibrium index* X , emerges well before the jammed state is reached; a rather subtle finding. This implies that the direct correlation function of a glass formed by supercooling a liquid (in which the molecules possess both repulsive and attractive interactions) provides a static growing length as its glass (jamming) transition is approached. Hence, our findings, based on nonequilibrium hard-sphere systems, could be applied more broadly to general glass formers, as we will elaborate below.

The present study focuses on prototypical glassy states represented by three-dimensional identical nonoverlapping spheres. For this system, it has been shown that MRJ packings are characterized by quasi-long-ranged pair anticorrelations in which $h(r)$ decays as $-1/r^4$ [11], reflecting an unusual spatial patterning of regions of lower and higher local particles densities relative to the system density. This particular quasi-long-ranged behavior of pair correlations for large r is equivalent to linear behavior in the structure factor $S(k)$ near the origin with $S(k)$ nonanalytic at $k = 0$. The structure factor $S(k)$ is defined in terms of the Fourier transform of $h(r)$, $S(k) = 1 + \rho \hat{h}(k)$, with ρ the number density, equal to $(6/\pi)\phi$ for unit-diameter hard spheres with packing fraction ϕ the fraction of space covered. Quasi-long-ranged anticorrelations have been shown to be present in the ground states of liquid helium [13] and noninteracting spin-polarized fermions [14], in the Harrison-Zeldovich spectrum of the early Universe [15], and in MRJ states of Platonic solids [16]. Experimentally, the most accurate measurements of the structure factor of bulk

amorphous silicon have revealed a linear trend in the small- k behavior of $S(k)$ toward $S(0) = 0$ that appears to be roughly consistent with hyperuniformity [17].

Linear behavior near the origin in $S(k)$ for a hyperuniform system indicates an inverted critical point [10], characterized by long-range anticorrelations in a direct correlation function $c(r)$ that decays as $-1/r^2$, where we define $c(r)$, via the standard Ornstein-Zernike integral equation, in terms of the Fourier transform of $\tilde{c}(k)$ as follows:

$$\tilde{c}(k) = \frac{\tilde{h}(k)}{S(k)} = \frac{S(k) - 1}{\rho S(k)}. \quad (1)$$

More information about this inverted critical point, including the associated critical exponents, can be found in Ref. [10].

II. SIMULATION PROCEDURE

In this work, we study million-particle packings of identical spheres overcompressed at various rates fast enough to avoid the formation of crystallites. We employ an event-driven friction-free Lubachevsky-Stillinger molecular dynamics protocol under periodic boundary conditions [18] in a cube of side length unity where initial sphere velocities are Maxwell-Boltzmann distributed such that mean energy per sphere (of mass unity) is $k_B T = 1/2$, where k_B is Boltzmann's constant and T is temperature. Simulations are performed to overcompress spheres from various initial states (including equilibrium liquid) at densities below freezing $\phi_f = 0.494$ up to various percentages of the jamming fraction ϕ_c . For each packing, ϕ_c is dependent upon initial conditions and compression rate, but it varies no more than 5×10^{-5} for packings compressed at the same rate due to the very large system size. We study rates in this work corresponding to sphere diameter growth per unit time from $\Gamma = 0.0007$ to $\Gamma = 0.03$ [18], where $\Gamma = 0.0007$ appears to be the slowest rate at which crystallites do not form.

We closely examine the small wavenumber k behavior of the angularly averaged structure factor $S(k)$, where k is the magnitude of a wavevector \mathbf{k} . We calculate $S(k)$ by direct Fourier transform, omitting forward scattering, for $N = 1,000,000$ spheres of diameter $D = 1$ in a periodic cube of length L replicated over all space, using the relation

$$S(\mathbf{k}) = (1/N) \left| \sum_{j=1}^N e^{i\mathbf{k}\cdot\mathbf{r}_j} \right|^2,$$

and angularly averaging over all \mathbf{k} of equal magnitude k . The smallest nonzero wavenumber $kD/2\pi$ calculated by this method is equal to D/L , which for 1,000,000 unit-diameter spheres at jamming is roughly 0.01. Figure 1 compares the behavior of $S(k)$ for (a) a single packing overcompressed from the equilibrium liquid at $\phi = 0.69\phi_c$ to $\phi = 0.9999999\phi_c$ and (b) an average of 20 independently generated packings in the equilibrium liquid state with $\phi = 0.45 \approx 0.70\phi_c$.

III. RESULTS AND ANALYSIS

In this section, we present our central results for packings of 1,000,000 spheres compressed from various initial conditions below the freezing density up to glass-forming densities. In

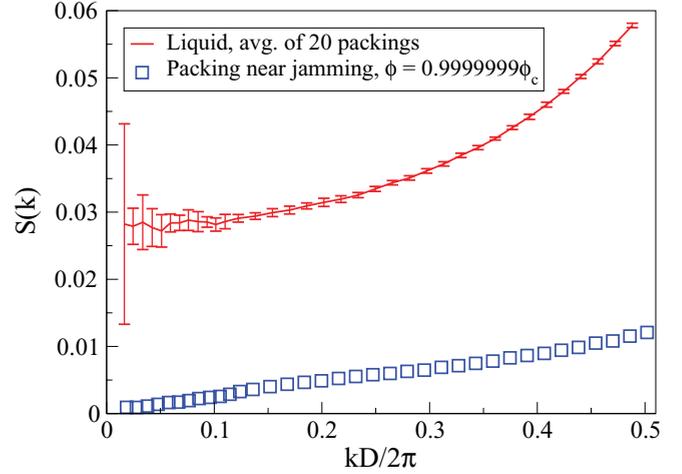


FIG. 1. (Color online) Bottom curve: angularly averaged $S(k)$ versus dimensionless wavenumber $kD/(2\pi)$ calculated by direct Fourier transform for a million-sphere packing with $\phi = 0.9999999\phi_c \dots$, with $\phi_c = 0.647032 \dots$ for this packing. Note the linear behavior in $S(k)$ as $k \rightarrow 0$. Top curve: average of 20 angularly averaged $S(k)$ calculated by DFT for independently generated million-sphere packings in the equilibrium liquid state with $\phi = 0.45$. Vertical bars represent an estimate of the standard deviation of the distribution of values for $S(k)$ at each k over the 20 packings.

particular, we identify a precursor to quasi-long-ranged pair anticorrelations present over a broad density range from just above freezing all the way up to jamming, manifest as linear behavior in $S(k)$, i.e., $S(k) = ak + b$. For ϕ greater than about $0.92\phi_c$, this behavior extends from the smallest k studied to about $k \sim 0.4$, whereas for $\phi_f < \phi < 0.93\phi_c$, a linear trend is clearly evident but does not extend to the smallest values of k for all compression rates studied. This behavior is illustrated in Fig. 2 for a wide range of densities [19].

Though plots of $S(k)$ from individual packings show variability at small k around the linear trend attributable to the dynamics of particle movements as the spheres are compressed, the average of several packings always illustrates a distinctly linear trend. This trend additionally appears for packings compressed at various rates from a random sequential addition (RSA) state [20], and the trend appears for packings compressed at fast but changing rates. Taken together, these observations indicate that the linear trend is easily reproducible across different compression rates and initial conditions, even nonequilibrium conditions like RSA, so long as the compression rate is fast enough such that crystallites do not form.

As $\phi \rightarrow \phi_c$, the values of $\tilde{c}(k)$ [Eq. (1)] near $k = 0$ grow very large. In particular, in the limit as $\phi \rightarrow \phi_c$ for a hyperuniform packing, $\tilde{c}(0) \rightarrow -\infty$. This behavior can be seen in Fig. 3, which are plots of $\tilde{c}(k)$ calculated using Eq. (1) and the fits in Fig. 2.

The length scale $\xi_{\text{DCF}} \equiv [-\tilde{c}(0)]^{1/3}$ grows continuously with packing fraction and diverges as the hyperuniform state is approached, indicating a long-ranged direct correlation function $c(r)$ that decays asymptotically proportional to $-1/r^2$. The growth in ξ_{DCF} signals the incipient rigidity associated with the formation of nearly jammed sphere-contact networks, and for hyperuniform MRJ packings, ξ_{DCF} diverges when the

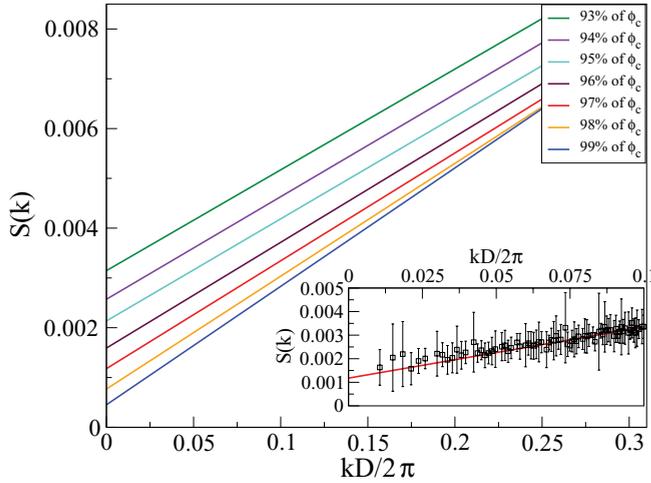


FIG. 2. (Color online) Linear fits of the structure factor $S(k)$ versus dimensionless wavenumber $kD/(2\pi)$ for various percentages of jamming fraction ϕ_c . The reported plots are generated from 20 angularly averaged structure factors $S(k)$ calculated by direct Fourier transform from million-sphere packings compressed at a rate $\Gamma = 0.03$ from the equilibrium liquid. For these packings, the smallest value of $kD/2\pi$ at which the structure factor is nonzero is 0.01070, corresponding to ϕ_c equal to about 0.6422. All fits achieve R -squared values greater than 0.995. The curves in the figure from top to bottom correspond to the labels in the legend from top to bottom. Inset: average data and estimate of the standard deviation (over the 20 packings) for angularly averaged $S(k)$ for packings compressed to $\phi = 0.97\phi_c$.

packing becomes completely rigid at the inverted critical point $\phi = \phi_c$. The presence of this inverted critical point suggests that renormalization group methods might be fruitfully applied to study the behavior of $c(r)$ in this and similar glassy systems.

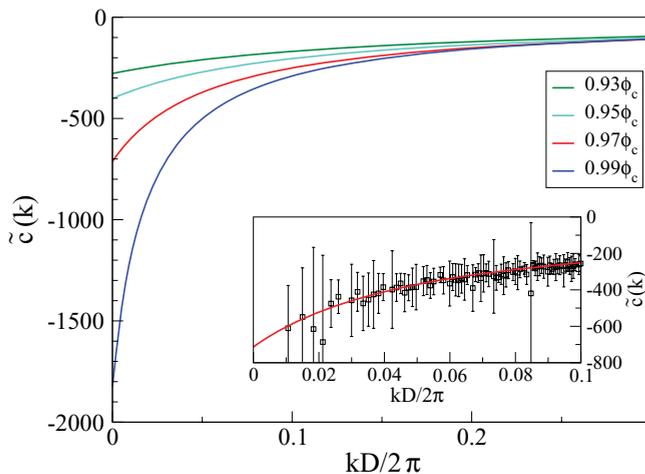


FIG. 3. (Color online) Fits of angularly averaged $\tilde{c}(k)$ versus dimensionless wavenumber $kD/(2\pi)$ calculated from the fits in Fig. 2. Note that $\tilde{c}(0)$ appears to diverge to $-\infty$ as $\phi \rightarrow \phi_c$. Inset: average data and estimate of the standard deviation (over 20 packings) for $\tilde{c}(k)$ for packings overcompressed to $\phi = 0.97\phi_c$. For this data set, geometric $[\mu_g = (\prod_{i=1}^{20} x_i)^{1/20}]$, with μ_g the mean and x_i the data points] and arithmetic averages were nearly identical.

In the mean spherical approximations [21], $c(r)$ can be thought of as the negative of an effective pair potential $v_{\text{eff}}(r)$, that is to say, $-\beta v_{\text{eff}}(r) = c(r)$ with $\beta = 1/k_B T$. Following this interpretation, MRJ packings exhibit long-ranged repulsions $v_{\text{eff}}(r)$ that are asymptotically proportional to $1/r^2$, which can be thought of as a generalized Coulombic interaction $1/r^n$ with $n = 2$ instead of $n = 1$, that drive the system to have no infinite wavelength density fluctuations, i.e., to be hyperuniform. In comparison, one-component plasmas in equilibrium interacting with a Coulomb potential [e.g., $v(r) \sim 1/r$ in 3D] are also hyperuniform [10,14,22].

Other quickly growing length scales can also be identified, e.g., the inverse of the first point k in $S(k)$ where linear behavior becomes dominant, which we term ξ_{SF} . This length scale is visually evident in $S(k)$ for the systems studied beginning at ϕ just above ϕ_f , and it can be shown [23] to correspond roughly to the point in sphere packings where $-1/r^4$ pair anticorrelations in $h(r)$ cease to be dominant and are supplanted by faster decay. This length scale ξ_{SF} grows far more quickly than ξ_{DCF} ; in particular, it is already greater than the size L of the million-sphere systems studied once $\phi = 0.93\phi_c$.

The identification of static growing length scales that can be extracted from pair information is a novel and unexpected finding. Though diverging time scales have long been evident in glasses, quickly growing length scales have been difficult to find. Recent studies have highlighted the presence of growing length scales using both static and dynamic four-point correlation functions; however, none of these length scales have been shown to grow very large, and it has been suggested that standard pair correlation functions may lack the information necessary to describe the static growing length scales present in glasses [24,25]. Our results demonstrate otherwise. By refocusing investigations to examining the small- k behaviors of $\tilde{c}(k)$ and $S(k)$, which are accessible to us via very large million-sphere packings, we are able to determine the large- r behavior of $c(r)$ and $h(r)$ (which is difficult to do in real space) to extract growing length scales.

Though there are growing length and time scales evident in the structure factors of these prototypical glasses, the packings are far from equilibrium. In particular, the compressibility equation for a many-particle system at number density ρ relating the isothermal compressibility $\kappa_T = (1/\phi)(d\phi/dp)_T$, with p the pressure, to infinite-wavelength density fluctuations,

$$S(0) = \rho k_B T \kappa_T, \quad (2)$$

which holds for systems in *thermal equilibrium*, does not hold for the nonequilibrium packings that we study in this paper. To investigate this concept further, we make use of an expression for the reduced pressure $p/\rho k_B T$ that is valid continuously from the freezing point ϕ_f to near the jamming density ϕ_c as obtained from the nearest-neighbor conditional pair distribution function $G(r)$ [26]. Though this expression is not exact for all values $\phi_f < \phi < \phi_c$, it does have the exact free-volume $1/(1 - \phi/\phi_c)$ behavior of the reduced pressure very near to jamming, and it has been shown to fit well to data over a broad range of ϕ [27]. The expression is

$$G(\infty) = p/\rho k_B T = 1 + 4\phi g_f(1) \frac{\phi_c - \phi_f}{\phi_c - \phi}, \quad (3)$$

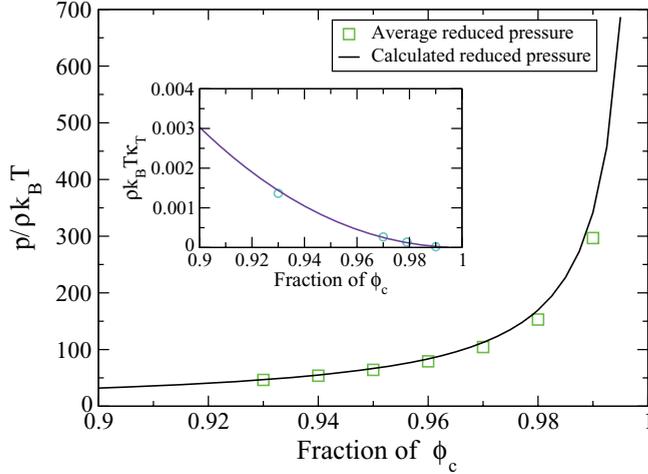


FIG. 4. (Color online) The dimensionless pressure versus percent of ϕ_c obtained by averaging over 20 packings compressed at rate $\Gamma = 0.03$ of reduced pressure at various percentages of ϕ_c , compared to the calculated values of reduced pressure from Eq. (3). Inset: average values of $\rho k_B T \kappa_T$ at each value of ϕ for four packings, compared to the calculated values using Eq. (4). The standard deviation of the measurement is about the size of the circle displayed for $\phi = 0.93\phi_c$ and much smaller than the circles for the other three measurements.

where $g_f(1)$ is the value of $g_2(1)$ for an equilibrium liquid at ϕ_f . From Eq. (3), we can derive the right-hand side of Eq. (2),

$$\rho k_B T \kappa_T = \frac{(\phi_c - \phi)^2}{4\phi\phi_c g_f(1)(\phi_c - \phi_f)}. \quad (4)$$

Our results, displayed in Fig. 4, show a good fit of Eq. (3) to the data over the values of ϕ studied in this work. Values of $\rho k_B T \kappa_T$ calculated from Eq. (4) also fit the data well. In Fig. 4, we calculate κ_T by rescaling velocities after each particle has undergone two collisions so that temperature remains constant. The expression $\rho k_B T \kappa_T$ is computed once every time particles have undergone 20 collisions each from the relation $\rho k_B T \kappa_T = (1/\phi)[\Delta\phi/\Delta(p/\rho k_B T)]$, with p the pressure, and the average over ten calculations is taken. The average of these values over five packings is reported as the measured isothermal compressibility. Though reduced pressure, and therefore κ_T , should change if spheres are allowed to relax (collide with no compression), in our simulations this change was undetectable within the error even for values of $\rho k_B T \kappa_T$ after relaxation times of 100,000 collisions per sphere at $\phi = 0.93\phi_c$.

With Eq. (4) in mind, we define

$$X \equiv \frac{S(0)}{\rho k_B T \kappa_T} - 1 \quad (5)$$

as a *nonequilibrium index* to quantify the degree to which the systems under study deviate from thermal equilibrium $X = 0$ [cf. Eq. (2)]. Figure 5 shows a plot of X versus ϕ , which demonstrates that X not only increases with increasing packing fraction ϕ , but that X diverges as $\phi \rightarrow \phi_c$.

Using Eq. (4) and fitting a linear trend to values of $S(0)$ with ϕ from Fig. 2 (inset of Fig. 5), the behavior of X as $\phi \rightarrow \phi_c$ for these systems can be calculated. Though both $\rho k_B T \kappa_T$ and $S(0)$ approach zero as $\phi \rightarrow \phi_c$, X still diverges with a pole

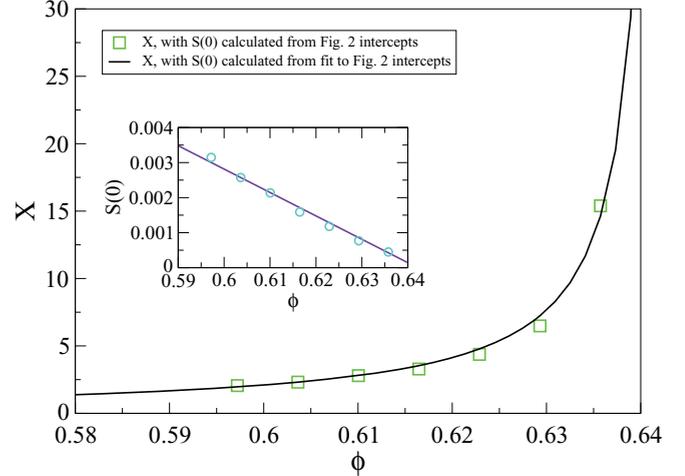


FIG. 5. (Color online) Plot of X versus ϕ , where $\rho k_B T \kappa_T$ is calculated from Eq. (4) and $S(0)$ taken from the linear fits in Fig. 2, compared to where $S(0)$ is calculated from a linear fit to the intercepts $S(0)$ in Fig. 2. Inset: linear fit to the intercepts $S(0)$ in Fig. 2.

of order one at $\phi = \phi_c$. This is a noteworthy result, and it strongly indicates that the jammed glassy state for this model is fundamentally nonequilibrium in nature, though at this time it is unclear precisely how X will behave near ϕ_c for other glassy states and hyperuniform systems.

IV. CONCLUSIONS AND DISCUSSION

We have shown that for a variety of monodisperse hard-sphere systems compressed at various rates from different initial configurations there is a precursor to the jammed glassy state evident far below the jamming packing fraction ϕ_c . This precursor appears as linear behavior in the structure factor $S(k)$ near $k = 0$ associated with a quickly growing length scale ξ_{SF} , and for hyperuniform systems is indicative of the onset of an inverted critical point at $\phi = \phi_c$ associated with a diverging length scale ξ_{DCF} and a negative, long-ranged power-law decay of the direct correlation function $c(r)$. In future work, it will be interesting to see whether renormalization group methods could be applied to study the behavior of $c(r)$ in the vicinity of the inverted critical point. Our identification of two nonequilibrium static growing length scales is a unique finding that demonstrates the onset of the jammed glassy state is detectable using standard pair information [28].

Due to the early onset and robustness of the jamming precursor and the dynamics employed in our model of a prototypical glass, we expect that our results are broadly applicable to glass forming molecular systems (e.g., metallic glasses, network glasses, etc.). Hard-sphere packings near jamming are known to provide excellent structural models of glassy molecular states [1,20,29]. Endowed with Newtonian dynamics and quickly compressed, hard-sphere models are driven by strong pair repulsion and free-volume dynamics, which are the salient drivers in their molecular counterparts. These drivers lead to diverging elastic moduli and time scales in our disordered hard-sphere packings just as sudden macroscopic rigidity and exponentially growing time scales appear in molecular glass formers. Therefore, the precursor to

the jammed glassy state and the growing length scales that we have shown to be present in hard-sphere glasses are applicable broadly to other glass formers [30,31], though it is not yet clear if these length scales are directly related to accompanying growing time scales and elastic moduli.

While we have demonstrated the existence of growing length scales that ultimately diverge at the critical state, we have also shown via a nonequilibrium index X that hard-sphere glasses are intrinsically nonequilibrium in nature, where X diverges as $\phi \rightarrow \phi_c$. It is an interesting question whether X will grow and become large with decreasing temperature as glassy states are approached in a model supercooled molecular glass. Indeed, in future work [32], we will demonstrate that the nonequilibrium index X has such

behavior, and we will additionally demonstrate the existence of accompanying growing static length scales analogous to the ones studied in this paper. All of these results support an alternative explanation for the nature of possible growing structural length scales present in a liquid upon supercooling and its transition to a glass, as noted in the Introduction.

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